PTO 04-4722

International Patent Publication
No. WO 95/03709

FLAVORING METHOD

Nicole Van Beem and Laurent Wuensche

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. AUGUST 2004
TRANSLATED BY THE RALPH MCELROY TRANSLATION COMPANY

WORLD ORGANIZATION OF INTELLECTUAL PROPERTY
International Office
INTERNATIONAL PUBLICATION NO.: WO 95/03709
INTERNATIONAL APPLICATION PUBLISHED IN ACCORDANCE WITH THE PATENT COOPERATION TREATY (PCT)

International Patent Classification[6]:	A 23 G 3/30 A 23 L 1/22
International Publication Date:	February 9, 1995
International Filing No.:	PCT/IB94/00227
International Filing Date:	July 26, 1994
Priority:	
No.:	2303/93-1
Date:	July 30, 1993
Country:	CH

FLAVORING METHOD

Applicant (for all designated states except US):	FIRMENICH S.A.
Inventors; and Inventors/Applicants (US only):	Nicole Van Beem and Laurent Wuensche

Designated States:	AU, BR, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE)
Published	With international search report.

FOR INFORMATION ONLY

Codes for the identification of PCT contract states on the cover sheets of the documents that publish the international applications in accordance with the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
EG	Egypt
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MZ	Mozambique
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
TZ	Tanzania
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Vietnam

Flavoring of chewing gums poses special problems in the food industry. The nature of /1* the substrate requires that the flavor be insoluble in water while being soluble in the base, thereby reducing loss of flavor by dissolution in saliva when the gun is chewed, and prolonging the flavoring effect. The flavor should also have good thermal stability so that it does not undergo degradation during the manufacturing cycle. This is why menthol, peppermint, and curly leaf mint are among the compounds of choice currently used for flavoring chewing gums. They are particularly appreciated for their refreshing minty effect together with good stability. However, the use of these flavoring ingredients requires doses that, in comparison with other common applications in the food industry, may seem particularly high. In fact, concentrations exceeding 0.1 – 0.2% and even more are not exceptional, hence the economic interest in replacing them, even partially, and improving their performance.

The process of the invention makes it possible to meet this twofold requirement.

The object of the invention is a process for increasing the flavor release properties of menthol, carvone, or eucalyptol, or by a natural or artificial flavoring composition containing them, in a product suitable for oral consumption, which process is characterized in that there is added to the product, which may or may not be previously flavored, a composition made of an inclusion complex of menthol, carvone, or eucalyptol, or a flavoring composition containing them, and β-cyclodextrin.

Another object of the invention is a chewing gum containing an inclusion complex made of menthol, carvone, or eucalyptol, or by a natural or artificial flavoring composition containing them, and β-cyclodextrin.

Although the principal object of the invention is a process for flavoring chewing gum, it may also be applied to other products for oral consumption, particularly products used for oral hygiene, where the active ingredients are released by chewing, rubbing, or brushing.

The state of the art abounds in examples of using cyclodextrins as encapsulating agents /2 for various volatile flavoring substances. Since their discovery, numerous applications have been reported in the literature. The essential point of the studies on cyclodextrins is that they mention the advantageous properties of these substances in comparison with active flavoring agents, properties that are expressed as better protection against oxidation, light, or heat, and loss to volatility or sublimation of these agents during storage.

Some particular applications have also been described in the patent literature. German Application No. DE-OS 2356098 describes a therapeutic preparation with analgesic and anti-inflammatory action made of a mixture of β-cyclodextrin, menthol, and methyl salicylate.

---

* [Numbers in the right margin indicate pagination of the original foreign text.]

Hungarian Patents No. 24895 and 59012 describe compositions for inhalation made of complexes of β-cyclodextrin with essences of eucalyptol or peppermint, camphor, and menthol.

Japanese Patent Application Nos. 61,197509 describes a liquid shampoo containing menthol and β-cyclodextrin, the latter being used to mask the unpleasant nature of the menthol.

Finally, French Patent Application No. 2666227 describes a composition for the treatment of oral infections; this composition is made of an inclusion complex of menthol with β-cyclodextrin.

Description of the invention

None of the references cited mentions or suggests the particular property of the inclusion complexes of β-cyclodextrin with menthol, carvone, or eucalyptol, a property that is the basis of this invention. In fact, we have discovered that these complexes have the property of reinforcing the flavor-releasing effect of the active ingredients, that is, menthol, carvone, or eucalyptol in their applications as flavoring agents for widely consumed products such as chewing gum, toothpaste, or oral hygiene products in general. This phenomenon is particularly pronounced in chewing gums. We have observed a similar effect with natural essences containing menthol, such as peppermint, as well as with carvone or curly leaf mint, and with eucalyptol.

Chewing gums generally consist essentially of a water-soluble part and an insoluble part /3
made of an elastic gum base to which a flavor is added.

The insoluble base is made up of elastomers, resins, fats, or oils, waxes, emollients and inorganic additives. Among the elastomers, which are present in a proportion of 10 to about 30% by weight of the chewing gum, we should also mention polyisobutylene, copolymers of isoprene and isobutylene, or styrene – butadiene, as well as natural latexes. The results, which are present in a proportion of about 15 to 30% by weight, are also of various kinds such as polyvinyl acetate and terpenic resins. It is customary to add emollients to this base to improve chewing and mouth feel. These may be glycerin, lecithin, or mixtures thereof.

None of the elements that make up the base seem a priori to have an affect on the phenomenon observed with the use of the complex containing menthol/carvone or eucalyptol/β-cyclodextrin, which is even more surprising.

Although similar effects have been observed with other α,γ, or modified cyclodextrins, it is preferable to use β-cyclodextrin. These commercial products are readily available on the market; the sources are Roquette Corporation, Gurnee, Illinois (USA) and RingdeX, Paris (France).

Inclusion complexes with the volatile active flavoring agent, whether menthol, carvone, eucalyptol, or essences that contain them, may be obtained by very simple mixing methods. For example, it may be indicated that β-cyclodextrin is to be mixed into an aqueous medium at a

concentration higher than the limit of its solubility. To this mixture, in paste form, we then add the required quantity of active flavoring ingredient, and the whole is then blended and filtered. Finally, the solid part is dried.

One alternative method consists of preparing an aqueous solution of β-cyclodextrin in a minimum volume of water and adding the active flavoring agent in the form of a solution in an inert organic solvent, for example ether, or in its pure form, for example for eucalyptol. When the addition is made, the resulting insoluble complex separates by precipitation, and is then collected by filtration or by decantation or centrifugation, and is finally dried. This last drying stage may be carried out by any common method: air drying, spray drying, atomization or aspiration under a vacuum. /4

The resulting complex can be added to the base made up of the mixture of various ingredients of the chewing gum during the mixing process, preferably during the last stage of manufacture. The quantities of the complex in the mixture may vary over a relatively wide range. In general, proportions on the order of 0.2% to about 6% by weight may be adapted for most of the applications envisioned. In these complexes, the proportion of flavoring agent may also vary depending on the nature of the agent and the desired flavoring effect. Concentrations of 10 – 15% by weight are considered, and are sufficient to promote a pronounced effect. As indicated above, the effect observed by the use of the complexes described is expressed as a substantial increase in the perceived coolness by an observer consuming an article flavored by these complexes. Although such a phenomenon is especially apparent in chewing gum, we have observed a similar effect in applications other than chewing gum, such as in the flavoring of tablets or toothpastes. Therefore, these are applications for which the active flavoring ingredient is released by the act of chewing or brushing of the matrix, which is made up of a solid or semi-solid substrate, as represented by a gum, a gel, or a toothpaste.

Embodiments of the invention

The examples of application described below illustrate the invention in more detail (temperature in degree centigrade).

Example 1

A chewing gum base is prepared by mixing the following ingredients (parts by weight):

Cafosa* Base (Dorada Plus T-205-01)	18.0
Sugar (50 μm)	61.5
Glucose 45° Bé	20.0
Glycerin 85%	0.5
Flavor	as needed

/5

Color if required

*Cafosa Gum Products Technology, Barcelona (Spain)

To manufacture a chewing gum in sticks, we proceeded as follows:

We placed the Cafosa base in a mixer preheated to 40°C. At this temperature, the base was heated for 5 min without being mixed. Then the heating was interrupted and the base mixed for 5 min. We added glucose, and the mixing was maintained for 2 min.

The sugar was then added in three successive fractions, mixing for 5 min after the addition of each fraction. After the second portion of sugar was added, we added the glycerin and the flavor and mixed the whole for 30 sec. Then we added the last portion of sugar and maintained the agitation for 5 min.

The resulting mass was laminated to a thickness of 1.5 mm with a Rondo rolling mill (Seewer AG), and during lamination, the mass was sprinkled with a mixture of 1/3 talc and 2/3 gelling sugar.

The resulting sticks were stored in the open for 48 h before they were sampled, and were then wrapped in aluminum foil.

By proceeding as indicated above, we prepared flavored sticks with the help of l-menthol used in a proportion of 0.2% by weight ("control" chewing gum) and sticks flavored with 1.66% of an inclusion complex of l-menthol/β-cyclodextrin, of which the l-menthol content was 12% ("test" chewing gum).

The taste evaluation by a panel of experts showed that the "test" sticks had a much more pronounced and refreshing menthol character than the "control" sticks.

When the chewing gum was flavored by the separate addition in identical proportions of β-cyclodextrin and l-menthol, the flavoring effect was comparable to that obtained by the addition of l-menthol alone.

When the complex 1-menthol/β-cyclodextrin is replaced by an inclusion complex made up of l-carvone/β-cyclodextrin, we also observed reinforcement of the flavor note of the l-carvone. The "control" sticks were prepared by the addition of l-carvone to the base in a /6
proportion of 0.1% by weight, while the "test" sticks were flavored with 0.9% of the complex l-carvone/β-cyclodextrin containing 11% l-carvone.

The same observations were made on the applications to anticaries, or sugarless gum.

The inclusion complex l-menthol/β-cyclodextrin used in the example described above was prepared as follows:

A quantity of 100 g of β-cyclodextrin was dissolved in 5.4 L of water. After nitrogen flush, a solution of 35 mL of diethyl ether containing 15g of menthol was introduced. the resulting mixture, under nitrogen, was agitated overnight. A white crystalline solid had formed,

and after decantation it was filtered. After it was washed and dried under a vacuum, we obtained 66 g of the desired complex with an l-menthol content of 12%.

Alternatively, this inclusion complex can be prepared as described below:

A quantity of 330 g of water was added to 200 g of β-cyclodextrin, and the mixture was cooled to 0° in an ice bath. Then the whole was mixed in an Ultra-Turrax, T-25 (IKA) dispersion apparatus for 5 min. A quantity of 24.8 g of finely ground l-menthol was then added to the mixture during mixing (10 min). After filtration, the separated solid was washed with 150 mL of water and then dried under a vacuum at 50°. In this case as well, the l-menthol content of the complex was about 12%.

Similar results were obtained when the drying was executed by atomization of the mixture obtained in water.

The βββ-cyclodextrin used in the examples described above was a commercial product with a purity of 99 ± 1% and a molecular weight of 1135 (origin: RingdeX, Paris, France).

Similar effects were observed by using partially methylated β-cyclodextrin in place of the β-cyclodextrin (for example, PMCD; origin: RingdeX) of which the methylation rate was 62.78%.

Example 2

We prepared a tablet base by mixing the following ingredients (parts by weight):

Cerelose Dextrose 02032[1)]	400.0
Cerelose Dextrose 02001	90.0
Flavor	as needed
Citric acid	as needed
Talc	6.5
Boeson VP[2)]	3.0
Magnesium stearate	0.5

/7

1) Cerestar AG, Herrligstr. 22, Zürich
2) Boehringer AG, Ingelheim/Rh.

The ingredients indicated were first sifted through a Frewitt apparatus with a pore size of 12-14 mesh, then mixed in a Hobart Planetary mixer for 5-6 min.

The resulting granular product was then compressed with a Fette Exacta 21 Eccentric apparatus. The resulting tablets had a weight of:

a. 900/1000 mg for chewable tablets, with a thickness of 4-5 mm, with a length of 16 mm and a width of 9 mm

b. 500/600 mg for tablets to be dissolved, with a thickness of 3-3.5 mm, a length of 16 mm and a width of 9 mm.

The flavor used consisted of l-menthol, used in a proportion of 0.1% for preparation of the "control" tablets, and an inclusion complex of l-menthol/β-cyclodextrin in a proportion of 0.9%, of which the l-menthol content was 11%, for preparation of "test" tablets.

A panel of experts asked to judge the taste of the tablets flavored in this way found that the "test" tablets had much more pronounced refreshing quality that the "control" tablets. This effect is not produced by separate addition of β-cyclodextrin and l-menthol to the base.

Example 3 /8

A base made up of a neutral-flavored commercial toothpaste gel was flavored with:

a. l-menthol in a proportion of 0.2% ("control" gel), and

b. an inclusion complex of β-cyclodextrin/l-menthol in a proportion of 1.66%, and of which the l-menthol content was 12% ("test" gel).

The panel of experts asked to judge the taste of the flavored gels prepared in this way stated that the "test" gel had much more pronounced refreshing effect than the "control" gel.

Example 4

A chewing gum base was prepared as indicated in Example 1. "Control" and "test" samples were flavored with peppermint essence in a proportion of 0.5% and a complex of β-cyclodextrin/peppermint in a proportion of 5%, in which the peppermint content was about 10%.

The panel of experts asked to judge the taste of the gums flavored in this way stated that the samples flavored with th complex β-cyclodextrin/peppermint had a powerful refreshing effect that was more pronounced than the effect of the samples flavored only with peppermint. When the peppermint was replaced by curly-leaf mint in the same proportions, the flavor-enhancing nature of the curly-leaf mint was reinforced.

Claims

1. Process to increase the flavor-releasing properties of menthol, carvone, or eucalyptol, or by a natural or artificial flavoring composition containing these, in a product suitable for oral consumption, characterized in that we add to said product, which may or may not be previously flavored, a composition made up of an inclusion complex of menthol, carvone, or eucalyptol, or a flavor composition containing them, and β-cyclodextrin.

2. Process according to Claim 1, characterized in that the product for consumption is a chewing gum.

3. Process according to Claim 1, characterized in that the product for consumption is an oral hygiene product.

4. Process according to Claim 1, characterized in that peppermint or curly-leaf mint are used as the flavoring composition.

5. Process according to Claim 1, characterized in that the inclusion complex of l-menthol/β-cyclodextrin has an l-menthol content of 10-15% by weight with respect to the total weight of said complex.

6. Chewing gum containing an inclusion complex formed from menthol, carvone, or eucalyptol, or by a natural or artificial flavoring composition containing them, and β-cyclodextrin.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB 94/00227

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23G3/30 A23L1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A23G A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 392 608 (THE PROCTER & GAMBLE COMPANY) 17 October 1990 see page 6, line 5 - line 13 see page 6, line 38 - page 6, line 54 see page 7, line 15 - line 19; exa[illegible]e 13	4,6
Y	PATENT ABSTRACTS OF JAPAN vol. 15, no. 385 (C-0871) 27 September 1991 & JP,A,03 155 753 (KANEBO LTD) 3 July 1991	1-6
Y	US,A,3 061 444 (W.I. ROGERS) 30 October 1962 see column 5, line 1 - line 75; examples 3,4	1-6

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 September 1994	23.09.94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Lepretre, F

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB 94/00227

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0392608	17-10-90	US-A-	5102564	07-04-92
		US-A-	5094761	10-03-92
		AU-B-	642867	04-11-93
		AU-A-	5317490	18-10-90
		CA-A-	2013487	12-10-90
		CN-A-	1046574	31-10-90
		EP-A-	0392606	17-10-90
		JP-A-	3019978	29-01-91
		US-A-	5234610	10-08-93
		AT-T-	107351	15-07-94
		CA-A-	2013486	12-10-90
		DE-D-	69009833	21-07-94
		EP-A-	0392607	17-10-90
		JP-A-	3014679	23-01-91
		AU-B-	642866	04-11-93
		AU-A-	5317290	12-09-91
		CN-A-	1054605	18-09-91
		JP-A-	3259986	20-11-91
US-A-3061444		NONE		
FR-A-2666227	06-03-92	NONE		
WO-A-9300018	07-01-93	US-A-	5165943	24-11-92
		AU-A-	2262292	25-01-93
		CA-A-	2111474	07-01-93
		EP-A-	0590085	06-04-94